

PERFORMANCE OF CATIONIC POLYACRYLAMIDES IN PAPERMAKING - FLOCCULATION, DRAINAGE AND RETENTION

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ABSTRACT

SUMMARY

Flocculation, drainage and retention were investigated with distilled water and industrial water. As expected, it was concluded that flocculation, drainage and retention are highly affected by the quality of the water and by the polymer characteristics, namely the charge density, the number of branches and the molecular weight.

Flocculation with distilled water shows that the floc size increases with the molecular weight and the degree of branching or/and charge density. The opposite occurs with flocs compactness.

Drainage tests show that the reduction of the polymer molecular weight or of the charge density increases the drainage time. However, for polymers with a high branching degree, a reduction of the drainage time is detected. An increase from 50% to at least 75% of PCC retention was achieved by adding any of the flocculants.

The flocculation results obtained with industrial water were similar to those of the tests carried out with distilled water, the difference being the optimum concentration of each flocculant. As for the results with industrial water, the polymers that exhibit the better performance are those with high molecular weight and branching. Polymers with low branching resulted in flocs not so resistant to shear and more fragile, thus affecting negatively drainage/retention.

Keywords: branching, flocculation, cationic polyacrylamides, charge density, PCC.

INTRODUCTION

Mineral fillers have long been used in papermaking, especially in printing and writing papers, as they add positively to sheet formation, brightness, opacity and printability, besides lowering furnish cost.^[1] The common of flocculation of these fillers is crucial in order to maximize their retention in the fibre web, due both to economic and environmental concerns. However, since retention has to be balanced with an adequate drainage of the wet web and a good formation of the paper sheet, fibre flocculation should be limited whereas flocculation of fine particles and retention additives should be maximized. In papermaking, cationic polyacrylamides are usually used as retention aids. The efficiency of these polymeric additives depends on several factors, namely flocculants characteristics (structure, molecular weight, charge density, and concentration), characteristics of the suspended particles, characteristics of the suspending medium (pH, conductivity, and ionic charge), contact time, turbulence intensity, among others.^[2]

Some contaminants from the white water affect the flocculants properties and the particles surfaces, decreasing the flocculation efficiency. Furthermore, the reuse of the water increases the accumulation of solids in the voids between fibres (fines, fillers and destabilized dissolved and colloidal material) decreasing the drainage rate and efficiency.^[3,4] Moreover, flocculant overconcentration can also be a problem in papermaking due to its significant negative effect on dewatering. A high degree of flocculation, resulting in large flocs, reduces drainage time because it is difficult to remove the interstitial water from these types of flocs. The flocs characteristics are of great importance to improve

drainage. The contact time between the furnish and the chemical additives must be also taken into account for the choice of the retention system. The long contact times can drastically reduce the effect of the flocculant and thus the process efficiency.^[2]

The polymer structure is another parameter that affects the flocculation, drainage and retention performance and thus the wet-end efficiency.

The authors have developed and presented in various publications^[2, 5] an experimental methodology to monitor and evaluate flocculation in turbulent conditions, which is based on the use of Laser Diffraction Spectroscopy (LDS).^[5] LDS not only allows the determination of the aggregate average size and size distribution, but gives also the mass fractal dimension of the flocs, d_F ,^[6, 7] which provides a means of expressing the compactness of an aggregate. For solid nonporous particles $d_F = 3$ and for porous particles $1 < d_F < 3$.^[7] Moreover, when aggregate restructuring occurs, the aggregate structure is no longer fractal. Restructuring takes place at large length scales and information about flocs structure is provided by the so-called scattering exponent, SE, that is also determined from the scattering pattern.

The objective of this study was to evaluate the influence of the molecular weight (MW), degree of branching and charge density of tailored-made cationic polyacrylamides (C-PAM's) on the retention and drainage performance and, simultaneously, to correlate the results with flocculation kinetics and flocs structure, making use of the flocculation tests previously performed. Moreover, the effects of flocculant concentration and flocculant contact time were investigated.

A dynamic drainage analyzer (DDA) for evaluating the permeability of the fibres mat with the flocculated fillers was used. Flocculation results were obtained by using the aforementioned light diffraction scattering (LDS) technique.

EXPERIMENTAL

Materials. For the experiments, a eucalyptus bleached kraft pulp was used. The length of the fibres was 0.574 mm (length weighted). The pulp suspension, refined up to 38° SR, was diluted to a consistency of 1% in both the distilled and the industrial water. Before use, the suspended material of the industrial water was removed by microfiltration. The main quantifiable difference is the ionic content of both the distilled and the industrial waters and, consequently, the value of the conductivity (Table 1). The ionic content was determined by Atomic Absorption Spectroscopy and by ion chromatography. A scalenohedral precipitated calcium carbonate (PCC) supplied by the industry was used as filler and a suspension with a concentration of 1% in industrial water was prepared. The median size of the PCC particles, measured by LDS, was 2.054 μm .

Six C-PAM emulsions, developed and supplied by AQUA+TECH, were used in this study: (i) E1, a linear polyacrylamide with high molecular and 45 (w/w) of charged groups; (ii) E1+, a low branched polyacrylamide with high molecular and 50 (w/w) of charge groups; (iii) E1++++, a high branched polyacrylamide with high molecular weight and 50 (w/w) of charged groups; (iv) E2, a linear polyacrylamide with medium molecular weight and 45 (w/w) of charged groups; (v) E2++++, a highly branched polyacrylamide with medium molecular weight and 40 (w/w) of charged groups; (vi) F1, a linear polyacrylamide with high molecular weight and 35 (w/w) of charged groups.

The cationic monomer in all of the polymers is dimethylamino-ethyl-acrylate. Flocculant solutions were prepared daily with distilled water at 0.1% (w/w).

Table 1- Characterization of distilled and industrial waters.

Water	Ionic content (mg/l)								Cond. ($\mu\text{S/cm}$)	PH
	Na ⁺	Ca ²⁺	Mg ²⁺	K ⁺	Al ³⁺	Cl ⁻	SO ₄ ²⁻	Br ⁻		
Distilled	0.003	0.054	0.004	0.222	≤ 0.244	≤ 20 ppb	≤ 60 ppb	≤ 100 ppb	4-8	5.1
Industrial	110	25	9	3	0.682	52	15	21	634	8.0

Methods

Drainage Evaluation. Drainage tests were carried out using the Dynamic Drainage Analyzer^[9]. This equipment measures drainage and simultaneously gives information about retention and wet sheet permeability. It consists of a drainage unit and a microprocessor with control for the vacuum, the shear and the addition of chemical during the test.

Pulp suspension was prepared by mixing 500 mL of the fiber suspension and 100 mL of the PCC suspension corresponding to 0.83% (w/w) of fiber, 0.17% (w/w) of PCC and 99% (w/w) of water. The mixture was added to the DDA vessel equipped with a 350 μm square openings wire. In this way, a solids concentration (PCC + fiber) of 10 g/L was reached. The vacuum was maintained at 30 kPa, and the stirring speed in the vessel was 800 rpm. The suspension of fiber and PCC was stirred during 2 minutes before the addition of the flocculant in an adequate concentration.

Drainage tests were performed in distilled water and industrial water and, for both, the optimum flocculants concentration was studied. In industrial water the performance of all polymers for a common concentration of 12 mg/g was also studied. For each experiment, the flocculant contact time varied from 30 to 90 s. A blank test, without flocculant, was carried out daily, as reference.

Determination of Retention. The wet sheets obtained from the drainage tests in the DDA were used to determine the fines and filler retention. The residues collected were dried at 105 °C to calculate the total solids retention. Afterwards, the samples were burned at 600°C during 16 h to determine the PCC retention degree.

Flocculation Tests. The flocculation of the PCC particles was monitored by measuring the size of the aggregates by LDS in a Malvern Mastersizer 2000. The methodology adopted to evaluate the flocculation kinetics and the flocs structure for various flocculant concentrations has been described in previous papers.^[2,5] The influence of the flocculant molecular weight, charge density, branching and concentration on flocculation kinetics and on flocs structure was previously studied for the polymers E1+, E1++++, E2++++ and F1 in distilled and industrial water.

The mass fractal dimension of the flocs during flocculation was computed from the scattering pattern (the negative slope of the log-log plot of the scattering intensity versus the wave number (q)) based on the Rayleigh-Gans-Debye theory.^[6] However, when restructuring exists it takes place at the larger length scales and the slope for the restructured aggregate is higher at low q (large length scale) compared to that at high q . Information about the large scale of the floc structures can be acquired as the slope of the scattering pattern at low q (the scattering exponent, SE).

RESULTS AND DISCUSSION

Drainage tests were performed for the flocculant concentration corresponding to the maximum flocculation, as determined by LDS. Table 2 presents a summary of the median size (d_{50}) and SE at the maximum of the kinetic curve of flocculation, for the tests with distilled water.

Distilled water

Table 2 - Flocculation results obtained by LDS in distilled.

Polymer	Concentration optimum (mg/g)	Maximum in the kinetic curve	
		d_{50} (μm)	SE
E1	8	450	1.59
E1+	10	270	1.59
E1++++	10	282	1.42
E2	8	50	2.19
E2++++	8	350	2.10
F1	8	190	2.25

The results obtained by LDS for the flocculant in distilled water revealed that the polymers with low molecular weight produced more compact flocs. The C-PAM's charge density has an opposite effect. The optimum flocculant concentration depends on the flocculation mechanism which can be

influenced by the molecular weight. Bridging is the dominant mechanism for high molecular weight polymers and the flocs are more open. For low molecular weight polymers patching is the ruling mechanism. High branching C-PAM's produced large and open flocs, with a reduced tendency to reflocculate after breakage. In addition, the kinetics of flocculation is promoted by polymer branching, except when the degree of branching is too high.

The drainage tests results show that the reduction of the polymer molecular weight increases the drainage time and the same occurs with the charge density, but the effect is not so evident. The flocculants with the best performance in terms of flocs size, resistance and drainage time were also tested in the DDA using industrial water (Table 4).

Table 3 - Results obtained by DDA for optimum flocculant concentration for several polymers in distilled water.

Polymer	Optimum concentration(mg/g)	Drainage time (s)		Permissivity (mBar)	
		30 s	90 s	30 s	90 s
Blank test		14		233	
Contact time		30 s	90 s	30 s	90 s
E1	8	7	7	181	186
E1+	10	8	8	187	198
E1++++	10	6	6	168	163
E2	8	11	11	220	226
E2++++	8	8	9	202	210
F1	8	8	9	195	213

Industrial water

The optimum flocculant concentration increased when using the industrial water. This is because with industrial water a larger amount of polymer is necessary to neutralize the charges in suspension that are adsorbed around the mineral particles.

Table 4- Flocculation results obtained by LDS in industrial water

Polymer	Common concentration (mg/g)	Maximum in the kinetic curve			Optimum concentration (mg/g)	Maximum in the kinetic curve		
		d ₅₀ (µm)	d _F	SE		d ₅₀ (µm)	d _F	SE
E1+	12	56	1.59	1.67	22	204	1.56	1.77
E1++++	12	95	1.49	2.05	26	292	1.66	1.86
E2++++	12	60	1.57	1.20	68	370	1.73	2.04
F1	12	94	1.47	2.02	28	181	1.58	2.41

The branching degree increases the optimum concentration, flocs size and compactness. The flocs are less open for the polymers with low molecular weight.

As an example, Figure 1 shows the drainage curves for E1++++ for the optimum flocculant concentration at 30 and 90 s in industrial water.

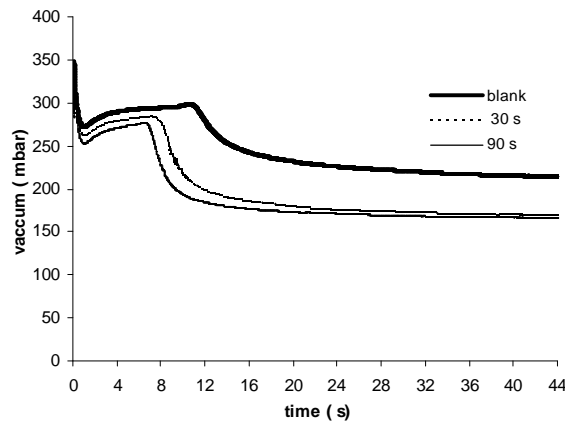


Figure 1- Drainage curves obtained for E1++++, for optimum flocculant concentration, 28 mg/g, and at 30 and 90 s in industrial water.

(The bold line refers to the blank test and the other lines refer to the drainage curve at 30 and 90 s.)

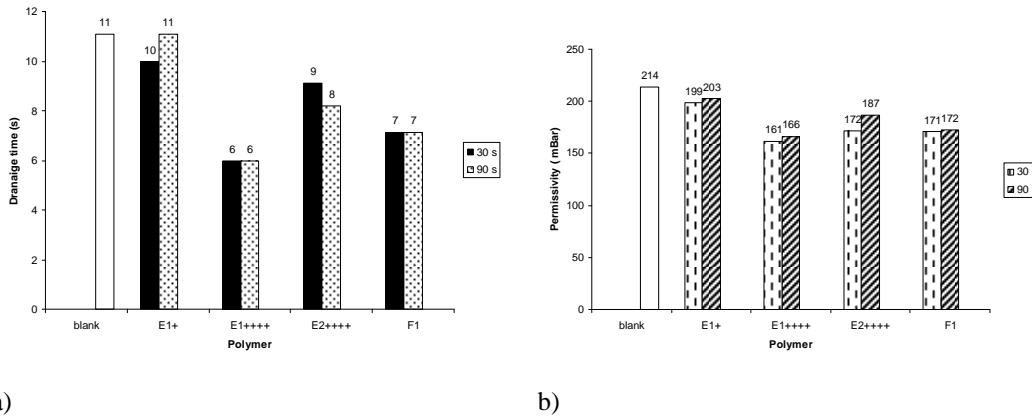


Figure 2 - DDA results for the common concentration (12 mg/g) a) Drainage time for industrial water b) Permissivity for industrial water.

Polymers with medium charge density but with high branching give better results. The relationship with the results obtained from flocculation (Table 4) shows that the E1++++ flocs' are open and larger than the F1 flocs', consequently the drainage time is lower for E1++++ (Figure 2).

Table 5 - Results obtained by DDA for optimum flocculant concentration for several polymers in industrial water.

Polymer	Optimum concentration (mg/g)	Drainage time (s)		Permissivity (mBar)	
		30 s	90 s	30 s	90 s
Blank test		11		214	
Contact time		30 s	90 s	30 s	90 s
E1+	22	19	14	201	193
E1++++	26	7	7	168	166
E2++++	68	∞	∞	282	290
F1	28	11	11	183	184

Besides, the optimum flocculant concentrations for E2++++ and F1 were very high leading to an increase of the suspending medium viscosity, and, consequently, to an increase of the drainage time and permissivity. Therefore, these concentrations resulted in overflocculation and produced too large flocs that reduce the drainage performance.

For E1++++ the amount of polymer was also high but the result was better than with the other polymers. The E1++++ formed opened flocs and it was easy to remove the interstitial water from this type of flocs (see Tables 4 and 5).

The common flocculant concentration (12 mg/g) gives better results than the optimum flocculant concentration. The flocs formed with the common concentration are smaller comparing to the flocs formed with the optimum concentration. In addition, the lower viscosity facilitated the drainage and retention process leading to a decreasing drainage time and promoting the high permeability. With this concentration it was also possible to minimize the problem of flocculant overdosage (see Figure 2 and Table 5).

Focussing on the results for the common concentration of 12 mg/g, it is apparent that polymers E1++++ and F1 performed better (Figure 2), leading to a lower drainage time. This result is consistent with the flocs characteristics (d_{50} , SE and d_F) presented in Table 4. These two polymers lead to medium size flocs for which the secondary aggregates are reasonably open ($SE \approx 2$), the same happening to the primary aggregate ($d_F \approx 1.5$). In the case of the other two polymers (E1+ and E2++++) both the flocs size and the SE and d_F values lead us to conclude that the flocculation degree is still low for this concentration. In fact, the secondary aggregates must be very weak and loose (very low SE), only primary aggregates being present which, for the low concentrations, are usually more compact. This explains also the smaller size of these flocs. Compact primary aggregates and weak secondary aggregates lead to high drainage times.^[3] Moreover, experimentally, it was detected that the E1+ flocs show low resistance to shear forces. After shearing, the broken percentage of the flocs was 9% both with the E1+ and E1++++ polymers, but reflocculation was very different: - 3% for E1++++ and -20% for E1+. The negative signal means that the flocs size still decreases after shear was ended. The flocculant contact time is also an important parameter but, with industrial water, there is no significant effect in drainage time or permeability.

Comparison between the results obtained with distilled water and industrial water

For the blank test the drainage time and permissivity decrease with the industrial water when compared with the distilled water. This decrease is due to the larger amount of ions contained in industrial water which contribute to the decrease of the thickness of the electric double layer around the particles and the fibres surface, allowing for the particles to get closer to each other and, thereafter, promoting aggregation.^[2, 9]

All the results obtained with the industrial water are quite distinct from those obtained with the distilled water.

A lower drainage time was expected for the E2++++ polymer in industrial water for the optimum concentration. However, viscosity becomes too high. For the common concentration, much lower than the optimum one, the flocculation degree must be too low. Furthermore, due to the high cationicity of the water this polymer tends to adopt a more coiled conformation, which disturbs permeability.^[9]

Retention. Table 6 shows the total and PCC retention for E1, E1+, E1++++, E2, E2++++ and F1 in distilled water and the results are very good, because has an increase of PCC retention of 50% to 97% is detected. All these flocculants act according to the bridging mechanism which leads to good retention.

Table 6 – Total solids and PCC retention in distilled water.

Polymer	Concentration optimum (mg/g)	Total solids retention (%)		PCC retention (%)	
		30 s	90 s	30 s	90 s
Blank test		88		50	
Contact time		30 s	90 s	30 s	90 s
E1	8	95	94	89	81
E1+	10	92	91	82	82
E1++++	10	97	97	86	86
E2	8	91	90	86	83
E2++++	8	98	99	97	91
F1	8	90	90	83	83

With the increase of molecular weight increases the probability of bridging to be the dominant flocculation mechanism. For the flocculant of high molecular weight (E1) the total retention and the PCC retention are very good because the flocculation mechanism is bridging. For E2 the molecular weight is smaller than for E1 the total retention and the PCC retention are lower. When the molecular weight decreases the PCC retention decreases as well. In general, retention increases with the number of branches, more notoriously in the case of the lower molecular weight polymers. The flocs obtained with E2++++ are larger than those obtained with the linear polymers and this is good for retention. When the molecular weight is lower, branches can improve the bridging mechanism.

The increase of charge density also influences the retention, which is smaller for F1 than for E1. This fact is understandable since the size of the flocs is larger with E1 than with F1, in spite of bridging being the ruling mechanism for both polymers.

An increase from 50% to at least 75% of PCC retention was achieved by adding any of the flocculants in Figure 3.

The retention with distilled and industrial water shows that the results are very different. Firstly, the total retention for the blank test is very similar for both but the PCC retention with industrial water is slightly lower than with distilled water (Table 7 and Figure 3). The results show that for the common concentration the polymer E1++++ gives better results.

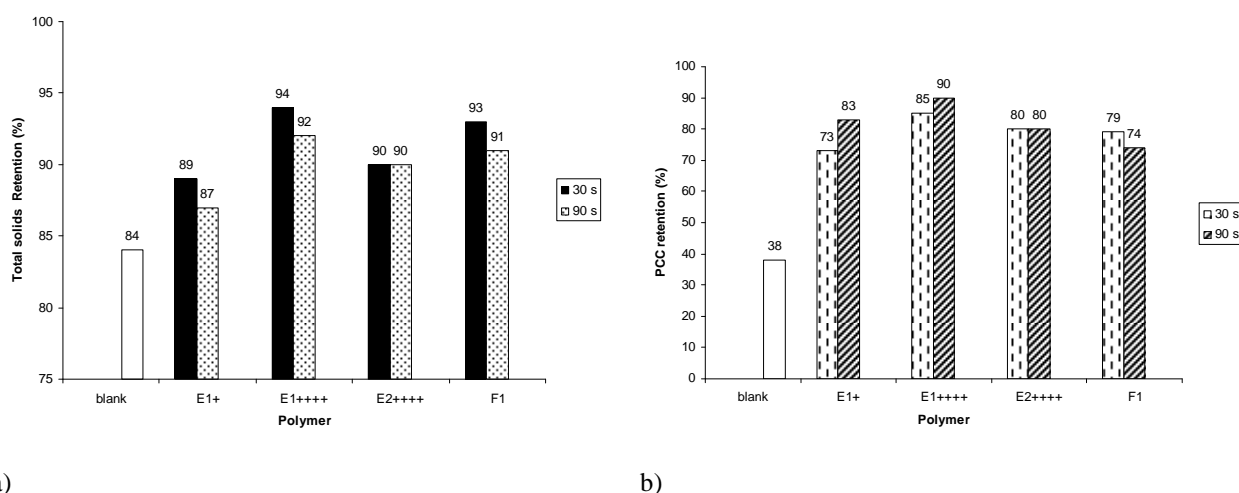


Figure 3 - Retention results for the common concentration (12 mg/g) a) Total solids Retention b) PCC Retention

For the optimum flocculant concentration most of the polymers give worse results due to overdosage and excess of flocculation, which produces large flocs and increases the drainage time. The only polymer that shows a good performance in industrial water for the optimum concentration is E1++++. The same happened for the lower concentration of 12 mg/g. Thus, it is worth to test this polymer further to decide about its possible use in paper manufacture.

Table 7 - Total and PCC retention in industrial water

Polymer	Concentration optimum (mg/g)	Total retention (%)		PCC retention (%)	
		30 s	90 s	30 s	90 s
Blank test		85		37	
E1+	22	86	91	67	68
E1++++	26	93	94	79	74
E2++++	68	88	91	41	41
F1	28	91	91	56	66

CONCLUSIONS

Polymer characteristics namely the charge density, the number of branches and the molecular weight affect the performance of flocculation, drainage and retention in papermaking. The flocculation in distilled water shows that the floc size increases with increasing the molecular weight. The polymers with low molecular weight produced more compact flocs. The flocs size increases with charge density. The increase of the branching degree influences the flocculation performance and produces larger and more open flocs. Drainage tests results show that the reduction of the polymer molecular weight increases the drainage time; the same occurs with the charge density.

The flocculation, drainage and retention in industrial water show that the polymer with the best performance is E1++++. A high concentration of the polymer increases the viscosity of the suspension leading to a high drainage time and a low permeability.

In industrial water the increase of branching influences the drainage time and permeability. The polymers with low branching formed flocs not resistant, affecting negatively the drainage and retention.

The polymer with a high branched structure and with a high molecular weight improves significantly the drainage rate and filler retention in comparison with the polymers with medium molecular weight and/or low branching.

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